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THE PROBLEMS OF STELLAR STRUCTURE

Part I

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The first application of New Quantum Statistics to Astrophysics was contained in a very suggestive paper by Fowler.[1] This has been followed by the work of Frenkel,[2] Stoner,[3] and others. Recently Milne[4] has incorporated the Fermi-Dirac statistics in his new attack on the fundamental problem of Stellar Structure which was initiated by Eddington in his well-known researches about a decade ago. These new results discovered by Milne are of great significance and wide application.

The purpose of this paper is to give a critical but brief discussion of the present position regarding the fundamental problem of the stellar structure Incidentally it also provides a necessary background for a previous paper in the Monthly Notices[5] and for subsequent papers that are to follow the present one.

The physicist's point of view has been somewhat emphasized. Some new points and results which naturally arise in such a discussion are given in the paper in their proper place and could hardly be conveniently summarized here.

This study in part was undertaken while at Cambridge, and it is a pleasure to express my grateful thanks to Professor R. H. Fowler and Professor E. A. Milne (Oxford) for their kind interest and many valuable suggestions. To professor M. N. Saha I am as ever grateful for the kind and continued interest that he has taken in my work.

§1. When we observe a star, we see a mass of material radiating in space. Its state appears to be constant in time.* For any star, there are, in principle, three "observables"—its "luminosity" L (which is the energy radiated per second),** its mass M and its radius r_1. Actually the radius has been determined directly, i.e., by measurement of the angular diameter and the parallax (which gives the distance of the star) in only a very few cases. But from a study of the stellar spectra, as interpreted by the theory of thermal ionization, the "effective temperature" T_e has been determined for many stars;*** the effective temperature being related to the radius r_1 according to the well-known relation $L = \pi a c r_1{}^2 T_e{}^4$, (a being the Stefan's constant and its value is 7.62×10^{-15} C. G. S. units).

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* Variable stars (Cepheids etc.) are excluded in the present discussion.

** The luminosity is usually stated in terms of the "absolute bolometric magnitude" M_{bol} which is connected with L by the well-known relation $Log_{10} L = -0.4 M_{bol} + 35.52$. (L in ergs/second).

*** For some very bright stars the effective temperature has also been determined by measuring the energy in different parts of the spectrum. The star is assumed to radiate as a black body and T_e is calculated by Planck's law. The values for T_e obtained by these and other methods are in good agreement (Russell, Dugan and Stewart, Astronomy, volume II, page 753).

The different stars vary very considerably in luminosity among themselves - the range of variation being of the order of 10^8.* The following table shows roughly the range of variation of the various physical quantities amongst different stars.

	Luminosity L	Mass M	Radius r_1	Effective temperature T_e	Mean density	Energy radiated
Order of magnitude of the range of variation	10^8	10^2	10^4	10 (From 3,000 to 30,000 deg.)	10^{12} (From 10^{-7} to 10^5 grm /c.c.)	10^6 (From 10^{-2} to 10^4 erg/grm. sec.)

It is now well known from the researches of Eddington and those of others that there exist correlations between the three observables L, M, and T_e. These correlations are perhaps best exhibited by plotting Log L, Log M, and Log T_e in a three-dimensional figure. The representative points of the stars are not distributed at random, but are very markedly localized in definite regions. This is shown (idealized) in figure 1. Speaking very roughly :

(*i*) The stars all lie in the diagonal plane ABCD (the white dwarfs are an exception; they possess for a given mass a much smaller luminosity than other stars of the same mass); and further, (*ii*) in this diagonal plane the stars generally lie *scattered* about the two diagonals.

The correlation (*i*) between mass and luminosity was first formulated by Eddington, and is called the "mass-luminosity law;" the correlation (*ii*) between luminosity and effective temperature is due to Hertzsprung and Russell. This relation is shown more significantly when Log r_1 is plotted against Log L (see, Milne, Halley Lecture, 1933).

* For Rigel β orionis—the brightest star known—L is 14,000 times that for the Sun, whereas for α-Proxima Centauri—which is probably the faintest known star—L is only 1/11,000 that for the Sun ; thus showing a range of variation of the order of 10^8 (Russell, Dugan and Stewart, Astronomy, volume II, page 635).
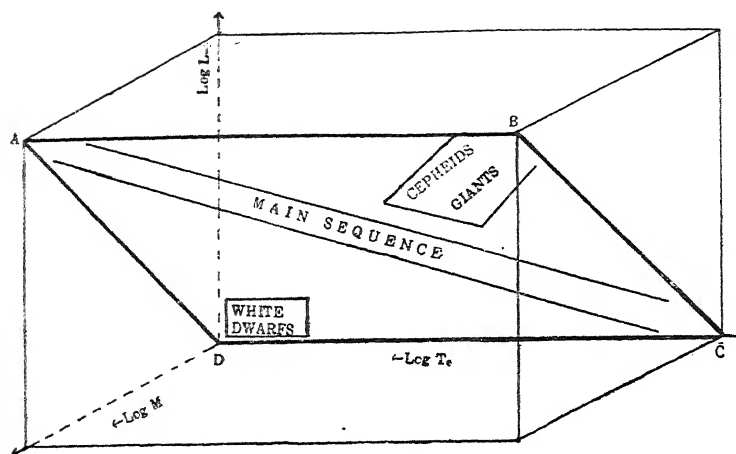
Fig. 1

These are the two fundamental relations which theoretical astrophysics has to explain.

The researches of Eddington, which on certain assumptions (the chief being that the star is entirely made of "classical" perfect gas) explained the "mass-luminosity-law," are now well known. The theory, however, was unable to offer any satisfying explanation of the "Russell-diagram." Milne, in his new attack on the problem of stellar structure, has obtained results which show the mass-luminosity law in a new light and afford at any rate a first clue towards the explanation of the broad features of the "Russell-diagram." However, for the sake of brevity (and perhaps also for clarity), we shall not follow here the line of historical development.

Ideally, the fundamental problem of stellar structure could be formulated thus :

For a given star of mass M (which is a spherically symmetrical aggregate of matter, calculate as to what will be (i) the luminosity (or luminosities) L; and (ii) the radius (or radii) r_1, making use of the following facts* known by observation :

(i) The star is in mechanical equilibrium because its state remains constant in time (for millions of years or longer) ;**

* See in this connection Milne, M. N. 90, 18, 1929.

** It is always understood that variable stars are excluded in the present discussion.

(*ii*) its outer layers are gaseous (in the sense of the "classical" perfect gas) as follows from the observed spectra ; and

(*iii*) its outer layers are in "radiative equilibrium." This is known from direct observation only in the case of the sun (from the observed variation of brightness over the solar disc), but it is plausible to assume it for all stars.

Equations of the Problem. —We now enumerate the fundamental equations of the problem :—

1. The equation of mechanical equilibrium is

$$\frac{dp}{dr} + \frac{dp_r}{dr} = -\frac{GM(r)}{r^2}\rho \qquad (1)$$

where p_r is the radiation pressure ($p_r = \frac{1}{3}aT^4$), p the gas pressure, ρ the density and $M(r)$ the mass enclosed within radius r. G is the gravitation constant.

Again we have* $$\frac{dM(r)}{dr} = 4\pi r^2 \rho. \qquad (2)$$

2. *The equations of heat flow and "heat equilibrium."* —The flow of heat is due to

(*i*) radiation,
(*ii*) conduction,
and (*iii*) convection.

It is usual in the investigations of stellar structure to assume that the convective flow is negligible.** Further, as shown by the author,[5] conductive flow is very small (when compared to radiative flow) in non-degenerate matter, but it is predominant when the degeneracy is intense.

If H_r denotes the net outward flow (per unit area and time) due to radiation, then

$$H_r = -\frac{c}{\kappa\rho}\frac{dp_r}{dr} = -\lambda_r\frac{dT}{dr} \qquad (3^1)$$

where κ is the radiative opacity and λ_r the "radiational conductivity" $\left(\lambda_r = \frac{4acT^3}{3\kappa\rho}\right)$. The heat flow due to conduction is

$$H_c = -\lambda\frac{dT}{dt}$$

λ being the thermal conductivity.

*This may be called the equation of the "conservation of mass."

This assumption has no strict physical justification. Rosseland (*M. N.* **89, 49, 192. *Zs. f. Astrophysik*, 4, 255, 1932) has often emphasized the importance of convection in stellar problems. However, the inclusion of convection would too much complicate the problem mathematically.

Combining these two we have

$$H = H_r + H_c = -(\lambda_r + \lambda)\frac{dT}{dr} = -\frac{c}{\kappa'\rho}\frac{dp_r}{dr}$$ (3¹¹)

Therefore,

$$\frac{c}{\kappa'\rho} = (\lambda_r + \lambda)/\frac{4}{3}aT^3 = \frac{\lambda r}{\frac{4}{3}aT^3}(1 + \lambda/\lambda_r)$$

or

$$\frac{c}{\kappa'\rho} = \frac{c}{\kappa\rho}(1 + \lambda/\lambda r)$$

and hence

$$\kappa' = \frac{\kappa}{1 + \lambda/\lambda r}$$

where κ' is called the "*effective opacity.*"

The equation (3¹¹) is identical with (3¹) except that the radiative opacity κ is replaced by the effective opacity κ'. In the sequel, we shall usually drop the dash of κ'.

If $L(r) = 4\pi r^2 H$, i.e., $L(r)$ is the net flux of heat crossing the sphere of radius r in an outward direction, then from (3¹¹)

$$\frac{dp_r}{dr} = \frac{\kappa L(r)}{4\pi cr^2}\rho$$ (3)

The equation of 'Heat equilibrium' is obviously

$$\frac{dL(r)}{dr} = \frac{d}{dr}(4\pi r^2 H) = 4\pi r^2 \rho\varepsilon.$$ (4)

where ε is the heat liberated per second per gramme in the material situated at radius r.

Little (or rather nothing) is known about the actual process of energy-generation that operates in the stellar interiors. The energy-generating process can be of various types. One may classify them as follows*:

(*a*) The rate of energy-generation is independent of the physical state** of the material, i.e., is a function of only C, where C is a parameter depending on the atomic composition of the material: $\varepsilon = \varepsilon(C)$.

(*b*) The rate of energy-generation depends on C as well as the physical state** of the material, i.e., $\varepsilon = \varepsilon(\rho, T; C)$.

(*c*) When the energy-generating process is in "temperature-equilibrium," then the forward reaction leading to energy-evolution and the reverse reaction leading to energy-absorption will be both proceeding simultaneously (and in fact, if the system be an enclosed one—thermally insulated—they both will

*See in this connection Note I at the end of the paper.

**This holds for the range of densities and temperatures that be under consideration ; for example, the energy generation by radioactive disintegration which ordinarily is of type (*a*) would very probably be of type (*b*) or (*c*) for very high temperatures of the order of 10⁹ degrees or higher.

proceed at exactly the same rate). For a process of this type "the energy-generation originates as an effect of the natural 'cooling' of the star by surface radiation to space; this causes adjustments in the interior which result in the liberation of energy by the slight excess of the reversible reaction going on in the direction encouraged by cooling."[6] The formula for ε will involve $\frac{dT}{dt}$ besides the physical parameters and C: $\varepsilon = \varepsilon \left(\rho, T, C, \frac{dT}{dt} \right)$.

(d) *Gravitational Contraction.*—As the star contracts, gravitational potential energy will be liberated for the star as a whole. However, for a given element of the mass, we cannot in the general case (where the law of internal distribution of density is changing as the star contracts) even fix the sign of the work done by gravity.

[For a perfect-gas star the energy evolved in any given element during homologous contraction under gravity is proportional to the temperature of that element.]

(e) *Nuclear β-ray capture and re-emission.*—Bohr[7] has recently drawn attention to the possibility of a far-reaching process involving a renunciation of the law of conservation of energy "If, in a collision process, an electron could attach itself to a nucleus with loss of its mechanical individuality, and subsequently be recreated as a β-ray (with the nucleus falling back to its initial state before the electron capture), we should find that the energy of this β-ray would generally differ from that of the original electron." This would imply a renunciation of the very idea of energy conservation.* Thus under some suitable (but yet unknown) conditions it may be possible for an assembly of electrons and atomic nuclei to *create* energy (for an indefinite time).[8]

If the possibility of this process were definitely established,** it would have revolutionary consequences on the whole problem of stellar evolution.

After this digression we revert again to the fundamental equations of the problem. To the above equations we add two more. A knowledge of the physics of matter at high temperatures and densities would give us

*To quote again from Bohr: "At the present stage of the atomic theory, however, we may say that we have no argument, either empirical or theoretical, for upholding the energy-principle in the case of β-ray disintegrations, and are even led to complications and difficulties in trying to do so."

**The recent great developments in the production of high voltages may also eventually lead to an investigation of the above process. An examination of the energy distribution of an intense beam of (artificially produced) β-rays scattered by atomic nuclei would reveal the presence of this process, if it occurred.

i) the 'equation of state' connecting p, ρ, and T, i e., $p = f(\rho, T; C)$,

ii) the equation expressing the opacity κ in the terms of ρ, and T, i.e.,
$\kappa = \kappa(\rho, T; C)$,

where C, as before, is the parameter depending on the atomic composition of the material.

Thus, the fundamental equations of the problem are

$$\frac{dp}{dr} + \frac{dp_r}{dr} = -\frac{GM(r)}{r^2}\rho \tag{i}$$

$$\frac{dp_r}{dr} = -\frac{\kappa L(r)}{4\pi c r^2}\rho \tag{ii}$$

$$\frac{dM(r)}{dr} = 4\pi r^2 \rho \tag{iii}$$

$$\frac{dL(r)}{dr} = 4\pi r^2 \rho\epsilon \tag{iv}$$

$$p = f(\rho, T; C) \tag{v}$$

$$\kappa = \kappa(\rho, T; C) \tag{vi}$$

and in the general case

$$\epsilon = \epsilon\left(\rho, T; \frac{dT}{dt}; C\right) \tag{vii}$$

The boundary conditions usual* in this problem are

(i) $\left.\begin{array}{l}\rho \to 0 \\ T \to 0\end{array}\right\}$ as $r \to r_1$ (r_1 is the radius of the star),

and (ii) $\left.\begin{array}{l}M(r) \to 0 \\ L(r) \to 0\end{array}\right\}$ as $r \to 0$.

It is of interest to note in this connection a very important theorem due to Vogt and Russell[9] which follows at once from (a mere inspection of) the above system of equations and boundary conditions. The theorem states that: Stars of fixed atomic composition and for which the process of energy-generation is of type (*a*) or (*b*) above, must exhibit not only an exact relation connecting

*Milne has recently examined (*Zs. f. Astrophysik*, 4, 75, 1932) the Schwarzschild boundary condition $T \to \{\sqrt{\tfrac{3}{4}}\}^{\frac{1}{4}} T_e$ as $r \to r_1$; and has obtained new and interesting results. However, we are not concerned with them here.

mass and luminosity, but similar exact relations between mass and radius, radius and effective temperature, and any other pair of their macroscopic properties.*

Now, in the Russell diagram connecting L and T_e, the stars—particularly the *giants* and the *supergiants*—are scattered so widely that there is obviously no hope of fitting all points on a simple curve as required by the above theorem. It may therefore be concluded, that either

> (i) the stars actually differ in chemical composition—atoms of various kinds being present in different proportions, either in the stars as a whole or from part to part of them,

or (ii) the energy-generating process is not of type (a) or (b), i.e., is not determined completely by ρ, T, and C,

[or both (i) and (ii) hold].

To a first approximation p and κ depend on C in only so far as the atomic composition affects the mean molecular weight μ (and generally under the conditions in the stellar interior μ is markedly sensitive only to the relative proportion of hydrogen, the proportion of other elements not affecting it very seriously). As regards ε, we can say nothing as to how it will depend on C. Further, as remarked before, ε will in general depend not only on ρ, T, and C, but also on $\dfrac{dT}{dt}$ (i.e., the specification of ε will not be complete unless we are also given the initial distribution of temperature inside the star—say at time t_0). Thus at the present stage it does not seem possible to specify the law of stellar energy-generation. In fact, progress in this direction is dependent not only on the advance in nuclear physics, but also primarily on our acquiring some definite knowledge regarding the order of temperatures and densities in the stellar interiors,** for only then is it possible to decide as to the type of the energy-generating process*** operative in the stellar interiors. *If this process be of type (c) or (d), then it will (essentially) be a problem for astrophysics alone to solve.*

Because of these considerations, it seems necessary to reformulate the fundamental problem (mentioned at the beginning of this section) in such a way that its solution does not depend on any theory of energy-

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*The assumption of fixed composition (i.e., C fixed) and the limitation of the type of the energy-generating process to (a) or (b) means that p, κ and ε are definite functions of ρ and T and do not involve any other arbitrary parameters.

**The current theories of stellar structure give widely different results.

***The different types of possible processes are mentioned above.

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generation.* Then, by comparing the solutions so obtained with the observed properties of stars, it would finally be possible to gain an "insight" regarding the mechanism of energy-generation.

§2. Following Milne, the problem is stated thus:

A star is observed to possess mass M and luminosity L; what are the possible steady-state configurations of spherically-symmetrical aggregates of matter possessing this mass M and luminosity L?

"To solve this problem we require a knowledge of the different phases which matter at a high temperature is capable of assuming. These phases include the "classical" perfect-gas and the degenerate-gas, both of them in the form either predominantly non-relativistic or predominantly relativistic; there may be, and probably are, other phases which are not yet known to us. The solution to the problem consists in enumerating in turn all the one-phase systems, the two-phase systems, the three-phase systems, and so on, consistent with the specification (L, M). L and M are selector variables, defining the configurations under discussion. When the enumeration has been completed as far as our present knowledge of different phases permits, comparison of the radius of the observed star (L, M) with the radii of the constructed configurations (L, M) will enable the state of the star to be diagnosed. If our knowledge of the different possible phases is complete, the constructed configurations must include amongst their number the actual configuration of the observed star (L, M)." (Milne, M. N., **92**, 612, 1932.)

The above programme requires no knowledge of the process of energy-generation.

So far, this programme has been carried out under some rather stringent simplifying assumptions for only one-phase gaseous configurations (Eddington) and two-phase configurations with gaseous envelope and (non-relativistic) degenerate core.[1] We now proceed to a brief consideration of these investigations.

Equations of the Problem.—

$$\frac{dp}{dr} + \frac{dp_r}{dr} = -\frac{GM(r)}{r^2}\rho \quad \dots \quad \dots \quad \dots \quad \dots \quad (5)$$

*The problem, therefore, can no longer be to calculate L for a star of given M, but to treat L, M, as independent variables and calculate all possible radii for given L, M.

$$\frac{dp_r}{dr} = -\frac{\kappa L(r)}{4\pi cr^2}\,\rho \qquad\qquad (6)$$

$$\frac{dM(r)}{dr} = 4\pi r^2\rho \qquad\qquad (7)$$

The boundary conditions are

$\rho \to 0, \quad T \to 0 \qquad$ as $r \to r_1,$ (the radius of the star)

and $\qquad M(r) \to 0 \qquad$ as $r \to 0.$

These equations have been already mentioned previously. From (5) and (6), we have

$$\frac{dp}{dr} = -\frac{GM(r)}{r^2}\,\rho\left\{1 - \frac{\kappa L(r)}{4\pi cG\,M(r)}\right\} \qquad\qquad (8)$$

Assuming that

(i) κ is constant, though not necessarily the same constant in each phase,

and (ii) $L(r)/M(r)$ is constant $= L/M$,

$$\frac{dp}{dr} = -\frac{GM(r)}{r^2}\,\rho\beta$$

where $\qquad\qquad \beta = 1 - \frac{\kappa L}{4\pi cGM}.$

These two assumptions are made for mathematical simplification.* Their usefulness resides in the circumstance that possible configurations can then be very largely worked out in full and that these may be used to yield insight into the nature of configurations for other laws of opacity and other (energy-generating) source-distributions. The "standard-model" is intended not to represent the stars in Nature, but to throw light on their structure.**

In the gaseous envelope

$$p = \frac{k}{\mu m_{\mathrm{H}}}\,\rho\,T, \quad \kappa = \kappa_1; \quad \beta_1 = 1 - \frac{\kappa_1 L}{4\pi cGM} \qquad\qquad (9)$$

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* Under these conditions, the three equations (5), (6) and (7) reduce to a single second order differential equation—the Emden equation.

** A star is said to be built on the "standard-model" when the above two conditions (i.e., $L(r)/M(r) = L/M$; $k = $ constant for each phase) are satisfied.

and in the (non-relativistic) degenerate phase

$$p = \frac{K\rho^{5/3}}{\mu^{5/3}}; \quad \kappa = \kappa_2; \quad \beta_2 = 1 - \frac{\kappa_2 L}{4\pi cGM} \tag{10}$$

where

$$K = \frac{8\pi h^2}{15m} \left(\frac{3}{8\pi m_H} \right)^{\frac{5}{3}}.$$

The pressure integrals — By division of (5) and (6) we have

$$\frac{dp}{dp_r} = \frac{dp}{d(\frac{1}{3}aT^4)} = \frac{4\pi cGM}{\kappa L} - 1$$

In any interval in which κ is constant, this integrates in the form

$$p = \frac{1}{3} aT^4 \left\{ \frac{4\pi cGM}{\kappa L} - 1 \right\} + D \tag{11}$$

where D is constant in the interval. D changes discontinuously from one constant value to another when κ changes.

Let D_1 be the value of D in the "classical" gas phase and D_2 its value in the degenerate phase   Using the boundary conditions

$$\rho \to 0, \ T \to 0 \text{ as } r \to r_1,$$

we find that $D_1 = 0$ and

$$p = \left\{ \frac{(k/\mu m_H)^4}{\frac{1}{3}a} \ \frac{1-\beta_1}{\beta_1} \right\}^{\frac{1}{3}} \rho^{\frac{4}{3}} = \triangle_1 \rho^{\frac{4}{3}} \tag{12}$$

where $\triangle_1$ is a constant.

Thus in the gaseous as well as the degenerate phase, p is connected with ρ by a relation of the form

$$p = \triangle \rho^\gamma \tag{13}$$

where $\triangle$ and γ are constants (different for each phase).

Reduction to Emden's Equation.—From (5), (8) and (13) we obtain

$$\frac{\triangle}{r^2}\frac{d}{dr}\left(\frac{r^2}{\rho}\frac{d\rho^\gamma}{dr}\right) = -4\pi G\beta\rho \qquad (14)$$

Further, on substituting $\rho = \lambda\Theta^n$ where λ is arbitrary, we have

$$\frac{n\gamma\triangle\lambda^{\gamma-2}}{r^2}\frac{d}{dr}\left(\frac{r^2\Theta^{n\gamma-1}}{\Theta^n}\frac{d\Theta}{dr}\right) = -4\pi G\beta\Theta^n$$

Choosing n such that

$$n = n\gamma - 1 \qquad \text{i.e.} \quad n = \frac{1}{\gamma-1} \quad \text{or } \gamma = 1 + \frac{1}{n}$$

we have

$$\frac{(n+1)\triangle\lambda^{\frac{1}{n}-1}}{r^2}\frac{d}{dr}\left(r^2\frac{d\Theta}{dr}\right) = -4\pi G\beta\Theta^n$$

Substituting

$$r = \xi\left\{\frac{(n+1)\triangle}{4\pi G\beta\lambda^{1-\frac{1}{n}}}\right\}^{\frac{1}{2}} \qquad (15)$$

we obtain the standard form

$$\frac{1}{\xi^2}\frac{d}{d\xi}\left(\xi^2\frac{d\Theta}{d\xi}\right) + \Theta^n = 0 \qquad (16)$$

(n is called the index of the Emden's equation).

Further from (8)

$$M(r) = -\frac{r^2}{G\beta\rho}\frac{dp}{dr} = -\frac{\lambda^{\frac{3-n}{2n}}}{2\pi^{\frac{1}{2}}}\left[\frac{(n+1)\triangle}{G\beta}\right]^{\frac{3}{2}}\xi^2\frac{d\Theta}{d\xi} \qquad (17)$$

By substituting the proper values for $\triangle$ and $\gamma = 1 + \dfrac{1}{n}$, we at once obtain for the *gaseous* phase,

$$\frac{1}{\xi^2} \frac{d}{d\xi} \left(\xi^2 \frac{d\theta}{d\xi} \right) + \theta^3 = 0 \tag{18}$$

$$\rho = \lambda_1 \theta^3 \tag{19}$$

$$r = \frac{\xi}{\lambda_1^{\frac{1}{3}}} \left[\frac{(k/\mu m_H)^4}{3a} \frac{1-\beta_1}{\beta_1^4} \right] \frac{1}{(\pi G)^{\frac{1}{2}}} \tag{20}$$

$$M(r) = - \left[\frac{16 (k/\mu m_H)^4}{\pi^{\frac{1}{3}} a G^3} \frac{1-\beta_1}{\beta_1^4} \right]^{\frac{1}{2}} \xi^2 \frac{d\theta}{d\xi} \tag{21}$$

where λ_1 is so far undetermined.

It follows that, that solution of (18) is required for which putting $M(r) = M$ in (21), at $\xi = \xi_1$, we must have

$$\theta = 0, \qquad \omega_3 \equiv - \xi_1^2 \left(\frac{d\theta}{d\xi} \right)_{\xi = \xi_1} = C^{-\frac{1}{2}}$$

where

$$C = \frac{16(k/m_H)^4}{\pi^{\frac{1}{3}} a \, G^3 M^2} \frac{1-\beta_1}{\mu^4 \beta_1^4} \tag{22}$$

and ξ_1 is arbitrary. The solution to be selected in the gas-zone thus depends solely on the physical properties in the gas-zone. If $f(\xi)$ is a solution of (18) vanishing at $\xi = \xi_0$ and satisfying $\omega_3 = C^{-\frac{1}{2}}$, then

$$\theta = A \, f (A\xi)$$

is the solution required where $A\xi_1 = \xi_0$.

For the *degenerate* phase, we have

$$\frac{1}{\eta^2} \frac{d}{d\eta}\left(\eta^2 \frac{d\psi}{d\eta}\right) + \psi^{\frac{3}{2}} = 0 \tag{23}$$

$$\rho = \lambda_2 \psi^{\frac{3}{2}} \tag{24}$$

$$r = \frac{\eta}{\lambda_2^{\frac{1}{6}}}\left[\frac{5K}{8\pi G \beta_2 \mu^{\frac{3}{3}}}\right]^{\frac{1}{2}} \tag{25}$$

$$M(r) = -\frac{\lambda_2^{\frac{1}{2}}}{4(2\pi)^{\frac{1}{2}}}\left[\frac{5K}{G\beta_2\mu^{\frac{3}{3}}}\right]^{\frac{3}{2}} \eta^2 \frac{d\psi}{d\eta} \tag{26}$$

where λ_2 is so far undetermined.

Before proceeding further, we may just note certain well-known properties of Emden's equation.

Proportion of Emden's Equation*.—Let $\theta = f(\xi)$ be a solution of Emden's equation of index n, vanishing at $\xi = \xi_0$. Then $\xi = \xi_1$ is the corresponding zero of the associated solution

$$\theta = A^{\frac{2}{n-1}} f(A\xi), \quad \text{if } A\xi_1 = \xi_0. \tag{27}$$

The value of

$$-\xi_1^{\frac{n+1}{n-1}}\left[\frac{d\theta}{d\xi}\right]_{\xi=\xi_1} \tag{28}$$

for any assigned member A of the family $\theta = A^{\frac{2}{n-1}} f(A\xi)$ is independent of the choice of A, for it is equal to

$$-\xi_0^{\frac{n+1}{n-1}} f'(\xi_0) \tag{29}$$

* These are here reproduced from Milne [4] *loc. cit.* page 618.

This is therefore a characteristic of the family, and its value may be taken to be the second arbitrary constant in the general solution. Denoting this constant by ω_n, the general solution may be written

$$\theta = A^{\frac{2}{n-1}} f(A\xi; \omega_n) \tag{30}$$

The value of ω_n identifies the homologous family under consideration.

It is known from the researches of Fowler and others that corresponding to an assigned zero $\xi = \xi_1$ of θ, for $\xi > 0$ there exists a critical $\omega^0{}_n$ of ω_n such that :

for $\omega_n = \omega_n^0$, $\theta(\xi) \to$ a finite limit as $\xi \to 0$ and $\theta(\xi)$ has no zeros in $0 \leq \xi < \xi_1$;

for $\omega_n < \omega_n^0$, $\theta(\xi) \to \infty$ as $\xi \to 0$ and remains positive in $0 \leq \xi < \xi_1$;

for $\omega_n > \omega_n^0$, $\theta(\xi)$ rises to a maximum as ξ decreases from $\xi = \xi_1$ and $\theta(\xi)$ then decreases to a zero lying in $(0, \xi_1)$.

There exists likewise a monotonic sequence of critical values $\omega_n^1 \, \omega_n^2$ $\ldots \omega_n^r \ldots$ such that for $\omega_n = \omega_n^{(r)}$, $\theta(\xi) \to$ a finite limit as $\xi \to 0$ and $\theta(\xi)$ has r zeros in $0 \leq \xi < \xi_1$.

When $\omega_n = \omega_n^0$, let θ_0 be the positive value to which θ tends as $\xi \to 0$, for any assigned value of A.

Then we have $$\theta_0 = A^{\frac{2}{n-1}} f(0; \omega_n'') \tag{31}$$

whence $$\xi_1^{\frac{2}{n-1}} \theta_0 = \xi_0^{\frac{2}{n-1}} f(0; \omega_n^0) \tag{32}$$

Thus $\xi_1^{\frac{2}{n-1}} \theta_0$ is the same for all members A of the homologous family $\omega_n = \omega_n^0$. We shall denote it by σ_n. We just note that[10]

$$\omega_n{}^0 = -\xi_0{}^2 f'(\xi_0); \; \omega^0{}_3 = 2 \cdot 0181; \; \omega^0{}_{\frac{3}{2}} = -\eta_0{}^3 \phi'(\eta_0); \; \omega^0{}_{\frac{3}{2}} = 132 \cdot 39$$

$$\sigma_3 = \xi_0 f(0); \; \omega_3{}^0 = 6 \cdot 8969; \; \sigma_{\frac{3}{2}} = \eta_0{}^4 \phi(0); \; \omega^0{}_{\frac{3}{2}} = 175 \cdot 23$$

Following the terminology of Milne, a solution $A^{n-\frac{3}{2}} f(A\xi; \omega_n)$ of

Emden's equation of index n, will be said to be of

$$\text{“Collapsed” type if} \quad \omega_n > \omega_n{}''$$
$$\text{“Emden” type} \quad \text{if} \quad \omega_n = \omega_n{}''$$
$$\text{and} \quad \text{“Centrally Condensed” type if} \quad \omega_n < \omega_n{}''.$$

§3. *One-Phase Gaseous Configurations.*—As in this case we are assuming the perfect gas phase to extend up to the centre of the star, the required solution of Emden's equation (index 3) must possess no singularity at the centre. The only such solution is the Emden solution ($\omega_3 = \omega_3{}^0$).

Therefore, from equation (22) we obtain

$$(\omega_3{}^0)^{-2} = \left(\frac{1}{2 \cdot 0181} \right)^2 = \frac{16 (k/\mu m_H)^4 (1-\beta_1)}{\pi^3 a G^3 M^2 \beta_1{}^4} \tag{33}$$

Hence,

$$1 - \beta_1 = 7 \cdot 82 \; 10^{-70} \; \beta_1{}^4 \; \mu^4 M^2$$

$$1 - \beta_1 = 0 \cdot 050 \; \beta_1{}^4 \left(\frac{M}{\odot} \right)^2 \left(\frac{\mu}{2 \cdot 1} \right)^4 \tag{34}*$$

where $\odot$ = mass of the sun.

Again we have

$$1 - \beta_1 = \frac{\kappa_1 L}{4\pi c G M}$$

Taking in accordance with Kramer's law),

$$\kappa_1 = \frac{\alpha_1 \; \rho_c}{T_c{}^{\frac{7}{2}}}$$

Where α_1 is a constant and ρ_c, T_c are the central density and central temperature respectively, we have

$$1 - \beta_1 = \frac{\alpha_1 \; \rho_c}{T_c{}^{\frac{7}{2}}} \; \frac{L}{4\pi c G M}$$

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* This is Eddington's famous quartic equation.

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Further from (11) we at once have

$$\frac{\rho_c}{\frac{1}{3}a T_c{}^3} = \frac{\beta_1}{1-\beta_1}\frac{\mu}{k/m_H}$$

and therefore

$$L = \frac{4\pi cGM}{\alpha_1}\frac{(1-\beta_1)^{\frac{13}{6}}(k/m_H)^{\frac{7}{6}}\rho_c^{\frac{1}{6}}}{(\frac{1}{3}a)^{\frac{7}{6}}\beta_1^{\frac{7}{6}}\mu^{\frac{7}{6}}} \tag{35}$$

From (19) and (20) and using the definition of σ_3 we find after a little reduction that

$$\rho_c = \frac{\sigma_3{}^3}{r_1{}^3(\pi G)^{\frac{3}{2}}}\left[\frac{(k/\mu m_H)^4}{\frac{1}{3}a}\frac{1-\beta_1}{\beta_1{}^4}\right]^{\frac{1}{2}} \tag{36}$$

Substituting this value of ρ_c in (35) and eliminating M by using (33), we have

$$L = 16\pi^{\frac{1}{4}}\ \omega_3{}^0\sigma_3{}^{\frac{1}{2}}\ \frac{(k/m_H)^{\frac{7}{2}}}{(\frac{1}{3}a)^{\frac{7}{4}}}\frac{c}{G^{\frac{3}{4}}}\frac{(1-\beta_1)^{\frac{11}{4}}}{\beta_1^{\frac{7}{2}}\mu^{\frac{7}{2}}}\frac{1}{(\alpha_1{}^2 r_1)^{\frac{1}{2}}} \tag{37}*$$

As from (34) β_1 is a function of $M\mu^2$, we can express (37) in the form—

$$r_1 = \frac{\text{constant}}{(\alpha_1 L)^2}f(M\mu^2) \tag{38}$$

For any prescribed (L, M) the uniqueness of the predicted radius is in conflict with the " Russell-diagram."

Further, when the theoretical value of α_1 is substituted in the formula and on the assumption that the stars do not contain a large proportion of hydrogen, the calculated value of r_1 comes out about a hundred times larger than the observed radius r_1 for any observed pair (M, L) selected from amongst the " ordinary " stars (i.e., not white dwarf stars) However, on the hypothesis of " hydrogen-abundance " these difficulties can be removed[11]. We shall not enter into this explanation here, but proceed to the two-phase configurations**.

§4   *Two-phase Configurations.*—We now consider the two-phase configurations of the "generalised standard model" consisting of a gaseous envelope and (non-relativistic) degenerate core.

*This is easily transformed in the more usual form, M_{Bol} = constant $- 3\cdot75$ Log $(1 - \beta_1)$ $- 3\cdot5$ log$M/\odot - 2$ log $\mu - \log T_e$. The effect of the last term is comparatively small so long as the effective temperature lies between about 3,000° to 25,000 degrees. This equation thus represents approximately (but not *exactly*) a relation between Mass and Luminosity. This is Eddington's "Mass-Luminosity law."

** According to Strömgren different types of stars imply varying amounts of hydrogen, so that the "hydrogen-abundance" is simply an empirical parameter which can be adjusted to fit with certain feature of the Russell-diagram.

Equations of Fit.—Though the actual transition from the perfect gas envelope to the degenerate central region must occupy a certain zone, we may for convenience take the two regions to be separated by a definite surface of demarcation.

We shall now obtain the equations that define the position of this interface.

In the following derivation, however, *we do not restrict to this particular case (of gaseous envelope and non-relativistic degenerate central region) but obtain the " equations of fit " in their most general form.*

Let the interface occur at $r = r'$.

Outside $r = r'$ let the distribution of density be given by a solution of Emden's equation of index n_1, and inside $r = r'$ let it be given by a solution of Emden's equation of index n_2. The fit of the "n_1-distribution" on to the "n_2-distribution" must be made in such a way that the mass missing from the incomplete "n_1-distribution" must be actually found in the incomplete "n_2-distribution".

Approaching the interface from the " " n_1-phase we have by (13), (14) (15) and (17)

$$ r' = \xi' \left[\frac{(n_1+1)\,\triangle_1}{4\pi G\beta_1\ \lambda_1^{\,1-\frac{1}{n_1}}} \right]^{\frac{1}{2}} \tag{39}$$

$$ M(r') = \frac{\lambda_1^{\frac{3-n_1}{2n_1}}}{2\pi^{\frac{1}{2}}} \left[\frac{(n_1+1)\,\triangle_1}{G\beta_1} \right]^{\frac{3}{2}} \ \xi'^2 \left(\frac{d\theta}{d\xi} \right)_{\xi=\xi^1} \tag{40}$$

$$ \rho_1' = \lambda_1 [\theta(\xi')]^{n_1} \tag{41}$$

$$ p' = \triangle_1 \rho_1'^{\left(1 + \frac{1}{n_1}\right)} \tag{42}$$

where ρ_1' is the density at the interface (it being approached from the "n_1-phase").

Approaching the interface from the "n_2-phase " we have similarly

$$ r' = \eta' \left[\frac{(n_2+1)\triangle_2}{4\pi G\beta_2\lambda_2^{\,1-\frac{1}{n_2}}} \right]^{\frac{1}{2}} \tag{43}$$

$$ M(r') = \frac{\lambda_2^{\frac{3-n_2}{2n_2}}}{2\pi^{\frac{1}{2}}} \left[\frac{(n_2+1)\,\triangle_2}{G\beta_2} \right]^{\frac{3}{2}} \eta'^2 \left(\frac{d\psi}{d\eta} \right)_{\eta=\eta'} \tag{44}$$

$$\rho'_2 = \lambda_2 \left[\psi(\eta) \right]^{n_2} \tag{45}$$

$$p' = \triangle_2 \rho_2'^{1 + \frac{1}{n_2}} \tag{46}$$

If $f(\xi)$ be a solution of Emden's equation (index n_1), $f\xi$ vanishing at $\xi = \xi_0$, then $A^{\frac{2}{n_1-1}} f(A\xi)$ is an associated solution having its zero at $\xi_1 = \xi_0/A$. Writing $A\xi = a$, we obtain after some reduction

$$r' = \rho_1'^{\frac{1-n_1}{2n_1}} \left[\frac{(n_1+1)\triangle_1}{4\pi G \beta_1} \right]^{\frac{1}{2}} a[f(a)]^{\frac{n_1-1}{2}} \tag{47}$$

$$M(r') = \frac{\rho_1'^{\frac{3-n_1}{2n_1}}}{2\pi^{\frac{1}{2}}} \left[\frac{(n_1+1)\triangle_1}{G\beta_1} \right]^{\frac{3}{2}} \frac{a^2 f'(a)}{[f(a)]^{\frac{3-n_1}{2}}} \tag{48}$$

Similarly if $\phi(\eta)$ be a solution of Emden's equation (index n_2), $\phi(\eta)$ vanishing at $\eta = \eta_0$, then $B^{\frac{2}{n_2-1}} \phi(B\eta)$ is an associated solution having its zero at $\eta_1 = \eta_0/B$. Writing $b = B\eta'$, we have corresponding to (47) and (48)

$$r' = \rho_2'^{\frac{1-n_2}{2n_2}} \left[\frac{(n_2+1)\triangle_2}{4\pi G \beta_2} \right]^{\frac{1}{2}} b \left[\phi(b) \right]^{\frac{n_2-1}{2}} \tag{49}$$

$$M(r') = \frac{\rho'_2^{\frac{3-n_2}{2n_2}}}{2\pi^{\frac{1}{2}}} \left[\frac{(n_2+1)\triangle_2}{G\beta_2} \right]^{\frac{3}{2}} \frac{b^2 \phi'(b)}{[\phi(b)]^{\frac{3-n_2}{2}}} \tag{50}$$

The conditions of fit are that the values of $M(r')$ and r' given by (47), (48) and (49), (50) shall be equal. Equating the values (and noting that the pressure must be equal on both sides of the interface) we have

$$\frac{1}{\rho'_1^2} \left[\frac{n_1+1}{\beta_1} \right]^{\frac{3}{2}} \frac{a^2 f'(a)}{[f(a)]^{\frac{3-n_1}{2}}} = \frac{1}{\rho_2'^2} \left[\frac{n_2+1}{\beta_2} \right]^{\frac{3}{2}} \frac{b^2 \phi'(b)}{[\phi(b)]^{\frac{3-n_2}{2}}} \tag{51}$$

$$\frac{1}{\rho'_1} \left[\frac{n+1}{\beta_1} \right]^{\frac{1}{2}} a \left[f(a) \right]^{\frac{n_1-1}{2}} = \frac{1}{\rho'_2} \left[\frac{n_2+1}{\beta_2} \right]^{\frac{1}{2}} b \left[\phi(b) \right]^{\frac{n_2-1}{2}} \tag{52}$$

By combining these two equations, they may be thrown in the "canonical form"

$$\frac{n_1+1}{\rho'_1 \beta_1} \frac{af'(a)}{f(a)} = \frac{n_2+1}{\rho_2' \beta_2} \frac{b\phi'(b)}{\phi(b)} \tag{53}$$

$$\frac{a[f'(a)]^n}{\rho_1 f'(a)} = \frac{b[\phi'(b)]^{n'}}{\rho_2 \phi'(b)} \tag{54}$$

These are the "equations of fit" in their most general form.**

For the case of the gaseous envelope ($n_1 = 3$) and (non-relativistic) degenerate interior ($n_2 = \frac{3}{2}$) the above equations reduce to

$$\frac{a[f'(a)]^3}{\rho_1 f'(a)} = \frac{b[\phi'(b)]^{\frac{3}{2}}}{\rho_2 \phi'(b)} \tag{55}$$

$$\frac{af'(a)}{f'(a)} = \left(\frac{\rho_1'}{\rho_2'}\right)\left(\frac{5}{8}\frac{\beta_1}{\beta_2}\right)\frac{b\phi'(b)}{\phi'(b)} \tag{56}$$

Further we may note that

$$1 - \frac{a}{\xi_0} = \frac{\text{Thickness of gaseous envelope}}{\text{Radius of configuration}} \tag{57}$$

Now from (15), after some algebra, we have for the total radius of the configuration

$$r_1 = \left(\frac{\rho_2'}{\rho_1'}\right)^{\frac{5}{3}}\frac{(\frac{1}{3}a)^{\frac{1}{6}}}{(\pi G)^{\frac{1}{2}}}\frac{K\xi_0 f'(a)}{(k/m_H)^{\frac{2}{3}}\mu(1-\beta_1)^{\frac{1}{6}}\beta_1^{\frac{3}{4}}} \tag{58}*$$

This transforms by using (55) and (56) and after some reduction into,

$$r_1 = \frac{5K/\mu^{\frac{5}{3}}}{2^{\frac{7}{3}}\pi^{\frac{2}{3}}GM^{\frac{1}{3}}\beta_2}\frac{\xi_0}{a}\left[\frac{-\xi_0^2 f'(\xi_0)}{a^2 f'(a)}b^5\phi'(b)\right]^{\frac{1}{4}} \tag{59}$$

In the sequel we shall assume the density to be continuous at the interface ($\rho_1' = \rho_2'$).**

If ρ' and T' denote the interfacial values of ρ and T, then

$$\frac{k\rho'T'}{\mu m_H} = \frac{K}{\mu^{\frac{5}{3}}}\rho'^{\frac{5}{3}} \tag{60}$$

Approaching the interface from the classical gas phase we have from (12)

$$\frac{kT'}{\mu m_H} = \left\{\frac{(k/\mu m_H)^4}{\frac{1}{3}a}\frac{1-\beta_1}{\beta_1}\right\}^{\frac{1}{3}}\rho'^{\frac{1}{3}} \tag{61}$$

Approaching it from the degenerate gas phase, we have from (11)

$$\frac{K\rho'^{\frac{5}{3}}}{\mu^{\frac{5}{3}}} = \frac{1}{3}a T'^4 \frac{\beta_2}{1-\beta_2} + D_2 \tag{62}$$

* As before, the pressure of degenerate gas is equal to $\dfrac{K\rho^{5/3}}{\mu^{5/3}}$

** Milne has given the "equations of fit" for this case of $\rho_1' = \rho_2'$. They are given here without this limitation.

Thus we obtain from (60), (61) and (62)

$$T' = \frac{(k/m_H)^{\frac{5}{3}}}{(\frac{1}{3}a)^{\frac{1}{3}} K} \left(\frac{1-\beta_1}{\beta_1} \right)^{\frac{2}{3}} \tag{63}$$

$$\rho' = \frac{(k/m_H)^4}{\frac{1}{3} a K^3} \frac{1-\beta_1}{\beta_1} \mu \tag{64}$$

$$D_2 = \frac{(k/m_H)^{\frac{20}{3}}}{(\frac{1}{3}a)^{\frac{5}{3}} K^4} \frac{(1-\beta_1)^{\frac{5}{3}} (\beta_1-\beta_2)}{\beta_1^{\frac{8}{3}} (1-\beta_2)} \tag{65}$$

The physical properties for the two phase configurations.

The solution $f(\xi, \omega_3)$ to be selected in the envelope depends solely on the "observables" L, M and κ_1 as

$$\omega_3 = C^{-\frac{1}{2}} = \frac{16(k/m_H)^4}{\pi^{\frac{1}{3}} G^3 M^2 \mu^4} \frac{1-\beta_1}{\beta_1^4}$$

and the solution $\psi(\eta, \omega_{\frac{3}{2}})$ must be the Emden-solution $(\omega_{\frac{3}{2}} - \omega^0{}_{\frac{3}{2}})$, because the non-relativistic degenerate phase is assumed to extend (in the physical sense) up to the centre.

From the equations already given, the formulæ for the various physical quantities - for example, the radius of the configuration, mean density, central temperature etc. — can be readily obtained. These can be expressed in terms of invariant form, a/ξ_0, b/η_0, $af(a)$, $b^4\phi(b)$, $-a^2 f'(a)$, $-b^5\phi'(b)$, so as to be independent of the "normalisation" to the zeros ξ_0, η_0. The values of a and b are found by solving the two equations of fit.

As an illustration we derive the formula for the central temperature T_c. From (62) and (65)

$$\frac{K \rho_c^{\frac{5}{3}}}{\mu^{\frac{5}{3}}} = \frac{1}{3} a T^4{}_c \frac{\beta_2}{1-\beta_2} + \frac{(k/m_H)^{\frac{20}{3}}}{(\frac{1}{3}a)^{\frac{5}{3}} K^4} \frac{(1-\beta_1)^{\frac{5}{3}} (\beta_1-\beta_2)}{\beta_1^{\frac{8}{3}} (1-\beta_2)} \tag{66}$$

Now

$$\rho_c = \lambda_2 [\psi(o)]^{\frac{3}{2}} = \lambda_2 B^6 [\phi(o, \omega^0{}_{\frac{3}{2}})]^{\frac{3}{2}} \tag{67}$$

and

$$\rho' = \lambda_2 B^6 [\phi(b, \omega^0{}_{\frac{3}{2}})]^{\frac{3}{2}} \tag{68}$$

Therefore

$$\frac{\rho_c}{\rho'} = \frac{(\sigma_{\frac{3}{2}})^{\frac{3}{2}}}{[\eta_0^4 \phi(b)]^{\frac{3}{2}}} \tag{69}$$

Substituting from (64) for ρ'

$$\rho_c = \frac{(k/m_H)^4 \mu}{\frac{1}{3} a K^3} \frac{1-\beta_1}{\beta_1} \frac{[\sigma_{\frac{3}{2}}]^{\frac{3}{2}}}{[\eta_0^4 \phi(b)]^{\frac{3}{2}}} \tag{70}$$

Therefore

$$T_c = \frac{(k/m_H)^{\frac{5}{3}}}{(\frac{1}{3} a)^{\frac{2}{3}} K} \left(\frac{1-\beta_1}{\beta_1} \right)^{\frac{5}{12}} \left(\frac{1-\beta_2}{\beta_2} \right)^{\frac{1}{4}} \left[\left(\frac{\sigma_{\frac{3}{2}}}{\eta_0^4 \phi(b)} \right)^{\frac{5}{2}} - \frac{\beta_1-\beta_2}{\beta_1(1-\beta_2)} \right]^{\frac{1}{4}} \tag{71}$$

Owing to the existence of the equations of fit, transformations of this formula are possible. It may thus be thrown in the form

$$T_c = \left[\frac{1-\beta_2}{\beta_2} \frac{K}{3a} \left(\frac{32}{125} \pi \frac{G M^2}{K^3} \left[\sigma_{\frac{3}{2}} \right]^{\frac{3}{2}} \beta_2 \mu^4 \right)^{\frac{2}{3}} \left(\frac{-a^2 f'(a) b \eta_0}{\xi_0^2 f'(\xi_0) b^3 \phi} \right)^{\frac{10}{3}} \right.$$

$$\left. - \frac{(k/m_H)^{\frac{20}{3}}}{(3a)^{\frac{8}{3}} K^4} \frac{1-\beta_1}{\beta_1^{\frac{8}{3}}} \frac{\frac{5}{3}}{\beta_2} \frac{\beta_1 - \beta_2}{\beta_2} \right]^{\frac{1}{4}} \tag{72}$$

The formulæ for the other physical quantities are given in Milne's paper and are also tabulated in my paper[5], where their applications are considered.

The solutions of the equations of fit (for the two-phase configurations) will give a and b as functions of β_1/β_2 and ω_3 (where ω_3 depends only on M and β_1). From equation (57) we have

$$\frac{\text{Radius of degenerate core}}{\text{Radius of configuration}} = \frac{a}{\xi_0} = F(\omega_3, \beta_1, \beta_2)$$

$$= F(\beta_1, \beta_1/\beta_2, M). \tag{73}$$

where $F(\beta_1/\beta_2, \omega_3)$ is known when the equations of fit have been solved. Milne has obtained by graphical methods the solutions of the equations of fit for a few values of ω_3 and has constructed curves for a/ξ_0, plotted against β_1/β_2 for constant ω_3. These are shown in figure 2 reproduced from Milne's paper.

Since
$$\frac{\beta_1}{\beta_2} = \frac{1-\kappa_1 L/4\pi c GM}{1-\kappa_2 L/4\pi c GM} = \frac{\beta_1}{1-\kappa_1/\kappa_2 (1-\beta_1)} \tag{74}$$

$\frac{a}{\xi_0}$ can be expressed as $F(\beta_1/\beta_2, M, \kappa_1/\kappa_2)$. Thus corresponding to any point $(\beta_1/\beta_2, \omega_3)$ in the figure, it is possible to find M for any given value of κ_1/κ_2. By joining up points of constant mass, we can describe on the diagram curves of constant mass M, for any given κ_1/κ_2, and so exhibit all the possible two-phase configurations of a given mass M. In order to gain any insight into these results for any value of κ_1/κ_2, Milne has examined in detail the limiting case of zero opacity in the core ($\kappa_2/\kappa_1 \sim 0$). And that this case has physical justification is easily seen as follows:—

Approximation for κ_2/κ_1. As an approximation, we shall take κ_1 the opacity in the envelope to be equal to the non-degenerate value at the interface, *i e.*, according to Kramer's law we take[5].

$$\kappa_1 = 4.23 \cdot 10^{25} \frac{\rho'}{T^{\frac{7}{2}}} \tag{75}$$

In the degenerate core, the heat flow would be predominantly by conduction[5] and so we shall take for κ_2 the value of the *'effective opacity'* (and not the pure radiative opacity) at the centre.

Now, as has been shown by the author,[5] the effective opacity is given by

$$\left(\begin{array}{c} \text{Effective opacity} \\ \text{at centre} \end{array} \right) = \left(\frac{\text{Radiative opacity } \kappa_2 \times \text{Radiational conductivity } \lambda_R}{\text{Thermal conductivity } \lambda} \right) \quad (76)$$

Therefore,

$$\frac{\kappa'_2}{\kappa_1} = \frac{\kappa_2 \text{ centre)}}{\kappa_1 \text{ (interface)}} \left(\frac{\lambda_R}{\lambda} \right)_{\text{centre}}$$

As $\kappa_2 \approx \frac{1}{T^2}$, and therefore κ_2 (interface) $> \kappa_2$ (centre) and hence

$$\frac{\kappa'_2}{\kappa_1} < \frac{\kappa_2 \text{ (interface)}}{\kappa_1 \text{ (interface)}} \left[\frac{\lambda_R}{\lambda} \right]_{\text{centre}}$$

Substituting the values for κ_2/κ_1 and λ_R/λ as given by equations (6 and 18) of my previous paper[5], we have

$$\frac{\kappa'_2}{\kappa_1} < \frac{6\cdot97}{A'_0} \cdot \frac{3\cdot88 \times 10^{-8} T_c I_1}{A_c^2} . \quad (77)$$

where A_c is the value of the Sommerfeld degeneracy-discriminant at the centre, and A_0' its value at the interface. The values of I_1 for different densities can be calculated from the formula given in the paper referred to and are tabulated therein.

At the interface the pressure given by the degenerate and the non-degenerate formulæ are equal,

$$\frac{K\rho'^{\frac{5}{3}}}{\mu^{\frac{5}{3}}} = \frac{kT'}{\mu m_H} \quad (78)$$

This gives by putting $K = \frac{8\pi h^2}{15m} \left(\frac{3}{8\pi m_H} \right)^{\frac{5}{3}}$,

the value of $A_0 = 2\cdot97$ at the interface.

Therefore

$$\frac{\kappa'_2}{\kappa_1} < \frac{9\cdot1 \times 10^{-8} T_c I_1}{A_c^2} \quad (79)*$$

and hence when the degeneracy at the centre is intense, i.e., $A_c \gg 1$, we can take

$$\frac{\kappa'_2}{\kappa_1} \sim 0.$$

* It may particularly be noted that this result essentially depends on our taking into account the conductive flow, i.e, on our using the " effective opacity", instead of the " radiative opacity."

As we are using non-relativistic statistics, the above formula is applicable as long as the relativistic effect is negligible and this is so provided $T \ll \dfrac{3\cdot57 \times 10^9}{A_c^{\frac{2}{3}}}$: substituting this value

for T_c, $\kappa'_c/\kappa_1 \ll \dfrac{3\cdot30 \times 10^2 I_1}{A_c^{\frac{2}{3}}}$.

Properties of Mass Curves for $\kappa'_2 \kappa_1 \sim 0$.—

We have in this case $\beta_1 \beta_2$ reduced to β_1. Some typical mass-curves are shown in the diagram. As we have already mentioned, a reasonable value for κ_1 is the value of the non-degenerate interfacial opacity. This gives

$$\kappa_1 = 10\cdot1 \, (M/L)^{\frac{4}{7}}$$
$$\text{and} \qquad 1-\beta_1 = 4\cdot01 \, 10^{-4} \, (L/M)^{\frac{3}{7}}$$

The horizontal scale of β_1 may thus be regarded as a scale of $(L/M)^{\frac{3}{7}}$ in the negative direction. The point E corresponds to $L/M=0$ and the configurations for the largest possible value of L/M occur in the region near the left-hand edge of the diagram.

Two types of mass-curves are seen in the figure. The mass-curve which separates the two types passes through the point A $(\beta_1=\frac{4}{5}, \omega_3=\omega_3{}^0)$, it is the curve $M=M_0$ where

$$\omega_3{}^0 = 2\cdot018 = \left\{ \frac{16(k/m_H)^4}{\pi^{\frac{1}{3}}aG^3M_0{}^2} \frac{(1-\beta_1)}{\mu^4\beta_1{}^4} \right\}_{\beta_1=\frac{4}{5}}^{-\frac{1}{2}} \qquad \dots \qquad \dots \quad (80)$$

$$M_0 = 2\cdot88 \odot \left(\frac{2\cdot1}{\mu} \right)^2 \qquad \dots \qquad \dots \qquad \dots \qquad \dots \quad (81)$$

From an inspection of the diagram it follows that :—

(i) For $M \leq M_0$, all configurations which exist are of collapsed type $(\omega_3 > \omega_3{}^0)$ and β_1 necessarily lies between $\beta_1{}^0$, and unity, where $\frac{4}{5} < \beta_1{}^0 < 1$, $\beta_1{}^0$ being a function of M given by

$$\omega_3{}^0 = \left[\frac{16(k/m_H)^4}{\pi(\frac{1}{3}a)9G^3M^2} \frac{1-\beta_1{}^0}{\mu^4(\beta_1{}^0)^4} \right]^{-\frac{1}{2}} \qquad \dots \qquad \dots \quad (82)$$

(ii) For $M > M_0$, the configurations which exist are either collapsed $(\beta_1 > \beta_1{}^0)$ or centrally condensed.

These two-phase configurations constructed by Milne, possess many striking properties. Consider a typical mass curve such as for $M=20\odot$. For this curve, any ordinate not too far to the left of S'T' (T' is vertically below S') meets the mass-curve in two points S, T. Thus for any assigned value of L/M exceeding that corresponding to the point T' (but not much exceeding it) and for the assigned mass M, there are two distinct configurations possible, of two different relctive core radii and accordingly two different external radii. Milne has suggested this phenomenon to be the counterpart of the existence in Nature of the two distinct giant M and B, O stars for large L/M. We thus at least gain some insight as to some features of the " Russell-diagram ". We shall, however, not enter here into these and other details, but shall merely note the explanation of the 'mass luminosity law' as given by Milne.
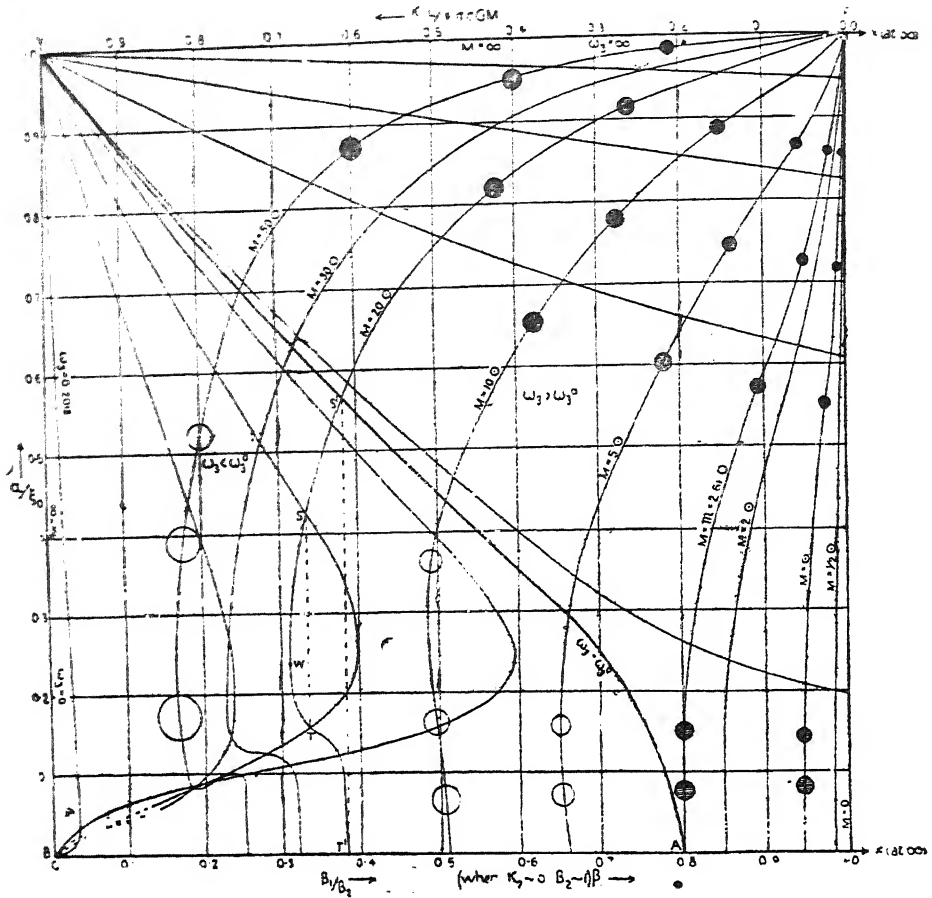
F. 4

FIG. 2—"*Curves of relative core-radius a/ξ_0 plotted against β_1/β_2 for constant ω_3. Also curves of a/ξ_0 against β_1 for constant mass M when $\kappa_2 \sim 0$, $\beta_2 \sim 1$. The locus $\omega_3 = \omega_3^0$ divides "centrally-condensed" configurations from "collapsed" configurations, and itself gives the quasi-diffuse configurations. The circles indicate qualitatively the external radii of the configuration; they are not drawn on a uniform radius-scale. Open circles denote "centrally-condensed" configurations, shaded circles "collapsed" configurations. Points such as W, represent configurations probably possessing Cepheid characteristics"* [From. Milne, M. N. 92, 630, 1932].

We see from the figure that for $M > M_0$, centrally-condensed portions of the mass-curves depart only slightly from the vertical. It follows that L must lie between narrow limits, depending on M, for a centrally-condensed configuration to be possible. "If L lies above these limits, no configuration exists, and the system would either burst or cease to be a two-phase system. If L lies below them, the system is collapsed with a large relative core-radius. We thus see that for $M > M_0$, the configurations

which are centrally-condensed will exhibit an approximate, but not exact mass luminosity correlation.

When $M \lessgtr M_0$, the lower parts of the mass-curves are also nearly vertical, so the smaller-cored collapsed configurations will also exhibit an approximate mass-luminosity correlation. Since the luminosity is in each case given approximately by

$$L = \frac{4\pi cGM (1 - \beta_1^0)}{\kappa_1}$$

it follows that the configurations in question, both for $M > M_0$, and for $M \lessgtr M_0$, will all obey the same mass-luminosity correlation. Thus the configurations we have held to resemble the B, O-stars, the giant red stars, and the main sequence of stars of nature all obey the same approximate mass-luminosity correlation. The configurations we have held to resemble the nuclei of planetary nebulæ and the white-dwarfs will depart from this correlation in the sense of possessing arbitrarily smaller luminosities for given mass" Milne, loc. cit., page 633.

A study of the physical properties, such as central temperature, etc., of the two-phase configurations with particular reference to white-dwarf stars has been made in the authors paper[5] already referred to.

As yet no systematic investigation of configurations with other-phase combinations have been made.

In the paper to follow, we shall consider non-relativistic degenerate and relativistic degenerate phase combinations.

Note I. A simple physical illustration of the three types of energy-generating processes discussed in the text:—

Consider a metallic bar of unit cross-section. Suppose it to be thermally insulated all round except at its two ends. Let one end be kept at 0^0 and the other end be enclosed in a thermally insulated chamber B.
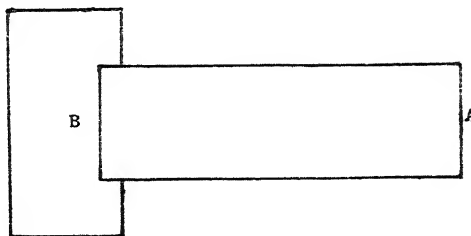

Fig. 3

Case (a). Let a unit mass of the energy-generating material be introduced in B (for example, a radioactive element). Then in steady-state, the heat flow H will be:

$$H = \varepsilon. \text{ (i)}, \qquad\qquad H = -\lambda \frac{d'T}{dr} \text{ (ii)}$$

and therefore T_B the (temperature of the end B) is $\varepsilon l / \lambda$, l being the length of the bar.

Case (b). Suppose that $\varepsilon = aT^s$

(For example, the energy source may be a resistance coil connected to constant voltage supply. The resistance and hence the heat generated will be a function of the temperature of the coil).

In steady-state

$$H = aT^s \qquad\qquad (i)$$

$$H = -\lambda \frac{d'T}{dr} \qquad\qquad (ii)$$

and hence

$$T_B = \left\{ \frac{\lambda}{a\,l\,(s-1)} \right\}^{\frac{1}{s-1}}$$

and

$$H = a \left\{ \frac{\lambda}{a\,l\,(s-1)} \right\}^{\frac{1}{s-1}}$$

Case (c). Introduce in B a reversibly reacting mixture in equilibrium $\left\{ A + \rightleftarrows AB + X \text{ calories} \right\}$. In this case we shall have no equation corresponding to (i) in the above two cases and hence H and T_B cannot be determined from steady-state considerations alone.

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ON THE ABSORPTION SPECTRA OF SOME SIMPLE SALTS OF THE TRANSITION ELEMENTS.

(CONTRIBUTION TO THE THEORY OF THE CO-ORDINATE LINKAGE, V[1])

BY S. MUJTABA KARIM AND R. SAMUEL.

The question of the colour of Inorganic salts of the transition elements has occupied the attention of many workers since a long time. In the more recent times G. Joos[2] has observed that these salts in solution have the same colour as that of their crystals. In general he concluded that the colour is due to aqua complexes formed by the water of crystallisation. He believed that the colour could not be due to the free metal ion because, he thought, that the term differences which were not very well known then, for the resonance lines of these would be very great on account of the high degree of ionisation, and therefore the absorption due to the Cations should be in the ultra-violet but not in the visible. Later White[3] gave a classification of the terms of Cr^{3+} ion. Saha then observed that some of the maxima in the violet and the green solutions of $CrCl_3$ were really in excellent agreement with the two deepest term differences of the Cr^{3+} ion as given by White. About the same time S. Kato[5] when taking preliminary absorption measurements came to the same conclusion. In the mean time H. Sauer[6] has shown that some complex Chromium compounds in the forms of alums at low temperatures (between -80°C and -180°C) show line absorption at about 6700λ which he ascribes to the complex $[Cr (H_2O)_6]^{3+}$. The absorption shifts to longer wave lengths with increasing temperatures. Joos and Schmetzler[7] have also found line absorption in the red region of the spectrum in a great number of Chromium complex salts at low temperatures. Recently D. M. Bose

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and collaborators have come to the conclusion that the absorption bands of some of these ions in solutions are in fair agreement with the known term difference of the free metal ions.

The ealier measurements being in many cases not quite satisfactory, the following piece of work was undertaken with a view to investigate the problem in detail on a wider experimental basis.

The absorption coefficients of the following salts in solution were measured:

VCl_3; Na_2CrO_4; $K_2Cr_2O_7$; $CrCl_3.6H_2O$; $MnCl_2$; $KMnO_4$; $FeCl_3.6H_2O$; $FeCl_2$; $CoCl_2.6H_2O$; YCl_3; $RuCl_3$; $RhCl_3.4H_2O$; $PdCl_2.2H_2O$; $OsCl_4$; $IrCl_4$; and $NiCl_2.6H_2O$.

The method of experimental procedure was the same as adopted by R. Samuel[9]. The solutions were prepared in the usual way in suitable solvents. It is thought desirable to add a few remarks about the behaviour and treatment of some of the salts.

VCl_3:—This substance was obtained by dissolving VCl_4 in water and leaving it for two days. Chlorine was given off and VCl_4 was turned into VCl_3.

It has a large hydrolysis and the solution contains also V_2O_3.

$CrCl_3.6H_2O$:—This substance gives a green and a violet solution. We have especially treated the green one. When one mole of the substance is dissolved in 100 litres of water, the amount of hydrolysis in the solution is to the extent of 9.4%. The green solution shows an equilibrium between $[CrCl(5H_2O)]$ Cl_2 and $[CrCl_2(4H_2O)]$ Cl ions, while the violet solution, obtained after keeping the green solution for some time, shows free Cr^{3+} and $3Cl^-$ ions.

$FeCl_3.6H_2O$:—It is a yellow very delequescent solid soluble in water. When 1 mole of the substance is dissolved in 6.4 litres the amount of hydrolysis is 2%, but it increases with dilution to 37% for one mole in 33.3 litres. The hydrolysis also increases with time, which seems to indicate the presence of $Fe(OH)_3$ ions in collidal form in water and therefore the different measurement can not be expected to show good agreement.

$OsCl_4$:—is strongly hydrolysed in solutions and contains a high percentage of $OsCl_5$. Therefore the results obtained are uncertain. $IrCl_4$ too is strongly hydrolysed in solutions.

$CoCl_2.6H_2O$: – The amount of hydrolysis is ·11% for one mole in 16 litres of water.

$NiCl_2.6H_2O$:– When 1 mole of the substance is dissolved in 35.2 litres of water the hydrolysis is· 3%.

YCl_3:––is soluble in water on the addition of a little HCl. When 1 mole of the substance is dissolved in 10 litres of water the amount of hydrolysis is ·01% at 16°C.

There is no hydrolysis in the solutions of Na_2CrO_4 and $K_2Cr_2O_7$, but the absorption spectra depends on the acidity of the solutions, as shown by Jander[10].

In the case of $MnCl_2$; $RuCl_3$; $RhCl_3.4H_2O$; $PdCl_2.2H_2O$; the amount of hydrolysis is very small. Similar is the case of $KMnO_4$ but it is sensitive to Organic impurities.

DISCUSSION

The results obtained are presented in the accompanying diagrams and tables and we shall proceed to discuss them. We shall treat in detail the results for the Chromium Chloride. The different solutions of this salt show maxima at 669, 632, 605, 527, 440 (470 till 410) and 280 mμ. In order to classify these we make use of the two older and more qualitative measurements of Bjerrum[11] and Byke and Jaffe[12]. These authors prepared different forms of Chromium Chloride with different amounts of water of crystallisation. This enables us to say by comparison of results that the maxima at 669mμ may be due to the ion $(Cr+6H_2O)^{3+}$, while those at 632mμ and 605mμ are due to $(CrCl_2+4H_2O)^+$ or $(CrCl+5H_2O)^{2+}$. The maximum at 527 mμ clearly belongs to the violet solution only, being stronger—in the m/100 and missing in the m/10 solution and can therefore be ascribed to $(Cr+6H_2O)^{3+}$ or Cr^{3+}. There remain only the two maxima at 440 mμ and 280 mμ for which we are not able to give a definite classification, but which we believe belong either to $(CrCl_2+4H_2O)^+$ or $(CrCl+5H_2O)^{2+}$.

If we compare these maxima with the term differences of the ion Cr^{3+}, it is interesting to find that just those maxima which on other and mainly chemical grounds we have attributed to the ion $(Cr+6H_2O)^{3+}$, agree with the lower term differences of the Cr^{3+} ion. These term differences are those to which Saha has already drawn attention viz $^4F - ^2G = 15014$ cms^{-1}, and $^4F - ^2H = 21027$

cms^{-1} (for the lowest component). These correspond to the maxima at 669mμ (about 15,000 cms^{-1}) and 527mμ (about 19000 cms^{-1}) the coincidance being quite satisfactory if it is remembered that the absorption maxima in solutions are always rather diffuse.

This coincidence was quite expected; but what is more surprising is the following relation. The maxima ascribed to $(CrCl_2 + 4H_2O)^+$ or $(CrCl + 5H_2O)^{2+}$ correspond to the deepest term differences of the spectra of the free Cr^+ and Cr^{2+} ions respectively. The ground term of Cr^+ is ^6S and the next term ^6D is only about 12500 cms^{-1} higher, so that the band corresponding to this term difference lies in the near infra-red and cannot be observed in our experiments. The next term difference, however, $^6S - ^2P$ is 16896 cms^{-1}, which agrees very well with the maxima at 632 or 605mμ (about 16000 to 16600 cms^{-1}). Similarly for Cr^{2+} the first term differences are $^3F - ^5D$, $^3G - ^5D$, and $^3F - ^3F$ with about 19000, 21000, and 38000 cms^{-1} respectively. Whereas the emission spectrum of Cr^3 accounts for two of the six absorption maxima only, the others are all accounted for by the term differences of Cr^{2+} and Cr^+. (see Table 1).

This remarkable coincidence if established, leads us to certain important conclusions. So an attempt at similar correlation was made for the absorption maxima of other salts. In this case, however, we meet with a certain handicap. Thus in the case of $MnCl_2$, nearly nothing is known about the spectrum of the free Mn^{2+} ion. The absorption maximum at 262 mμ (about 38000 cms^{-1}) coincides very well with the second deepest term difference $^7S - ^7P = 38366$ cms^{-1} of Mn^+, but we are not able to show definitely, for want of data, that it does not belong to some deep term difference of Mn^{2+}. A solution of $KMnO_4$ was treated with H_2SO_4 and H_2O_2 to study the absorption spectrum of $MnSO_4$. This curve shows that the maximum at 262 mμ of $MnCl_2$ has disappeared in the case of $MnSO_4$, where there is no possibility any longer for compounds like $[MnCl + 5H_2O]^+$.

In the same way the absorption maxima in the solution of $FeCl_3.6H_2O$, corresponds quite well with the Fe^+ spectrum (See Table IV for deatils); we cannot check the correspondence with Fe^{3+} because the latter spectrum is not analysed. Similar remarks hold good in the case of $CoCl_3.6H_2O$, where only Co^+ spectrum is known; the first term difference which lies in the visible can be found again in the absorption spectrum of the $CoCl_3.6H_2O$, but there is no possibility now of comparing the result with the Co^{2+} spectrum. The case of $PdCl_2.2H_2O$ is similar, (See Table VII).

Still more interesting is the absorption spectrum of $NiCl_2.6H_2O$. If we include the measurements of Dreisch[5] in the Infra-red with ours we see that the first four term differences of Ni are in nearly perfect agreement with the four absorption maxima of $NiCl_2$. But here also the absorption maxima cannot be compared with the spectrum of Ni^{2+} which is not known. (Table VI)

The case of YCl_3 is slightly different. This shows an absorption maximum at 265 mμ (about 38000 cms^{-1}). The ground term of Y^{2+} is ^2D; the next term is ^2S being 7966 cms^{-1} higher up; the term difference gives a line in the Infra-red; the next higher term is ^2P which is 44404 cms^{-1} higher than the ground term. We see, therefore, that the absorption maximum at 265 mμ can be indentified satisfactorily with this term difference. The spectrum of Y^{3+} is not yet analysed, but it can be readily seen that this spectrum will be analogous to that of Rb^{2+} or Na^{2+}. The excitation of Y^{3+} i.e. the fourth electron of Y means already the excitation of an electron in the next closed shell. So the spectrum of Y^{2+} will have none of its deeper term differences in the visible or the near ultra-violet. In a certain sense, therefore, the correlation between the spectrum of Y^{2+} and the absorption maximum YCl_3 may be said to have been directly established, the more so because the small amount of hydrolysis shows that the spectrum belongs really to the YCl_3.

The main results may be summed up as follows:—

(A) The coincidence which was first pointed out by Saha and later on by Bose between the absorption maxima and the term differences of the ions supposed to be in the solutions in the case of $CrCl_3.6H_2O$ and YCl_3 is verified by these experiments.*

(B) In the case of $CrCl_3.6H_2O$ where the specturm of Cr^+, Cr^{2+}, and Cr^{3+} are all known, we find that there are other maxima of absorption which coincide with the deepest term differences of Cr^{2+} and Cr^+, in addition to these which correspond to those of Cr^{3+}.

(C) Such coincidences between the absorption maxima and the deeper term differences of the ions in less ionised states than are originally supposed to be in the solution is also found in the case of $MnCl_2$; $FeCl_3.6H_2O$; $CoCl_2.6H_2O$; $NiCl_2$.
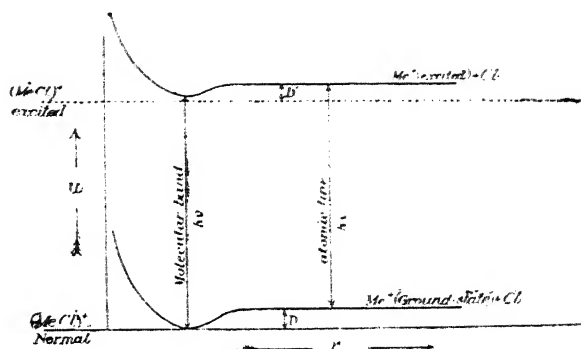
* We are not able to agree with the conclusions of Bose about the Ti^{3+} ion, because the absorption maximum of $TiCl_3$ although it agrees with certain term differences of the Ti^{2+} neither of these two is the ground term. The difference between the deepest of the levels and the ground level is 24 volts and it is difficult to believe that the ion can come directly in this excited state.

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$6H_2O$; YCl_3; and $PdCl_2.2H_2O$. In these six cases, however, the spectrum of the ion supposed to be in the solution are not analysed and so it is not possible to check the results. But the number of cases in which we find the coincidences mentioned above is sufficiently large to believe that the coincidences are not fortuitous.

(D). In two of these six cases, viz. $MnCl_2$ and YCl_3 we have been able to offer indirect evidence, mostly chemical in the first salt and spectral, by estimation of the deepest term difference, in the second case to show that the coincidence mentioned in (C) is rather real.

With all due reservations, therefore, we feel we are justified in discussing in detail some of the consequences of these results.

Making use of the qualitative measurements of some of the chemists it has been shown that in the case of the solutions of Chromium salts studied, the ion $(Cr+6H_2O)^{3+}$ exhibits absorption maxima which correspond to the spectrum of Cr^{3+} ion. Similarly the ions $(CrCl+5H_2O)^{2+}$ and $(CrCl_2+4H_2O)^+$ show absorption maxima which belong to the spectra of Cr^{2+} and Cr^+. This in itself is an interesting fact. In former communications of this series of contribution it was observed that the absorption maxima of e. g. the Hexacyanides of the same transition elements shared no such correspondence with the spectra of the free metal ions. The present fact may be taken, therefore, as an argument in favour of ascribing different kinds of linkage to the genuine complexes like the Cyanides mentioned and those loose complexes formed by the metal in association with the solvent. We shall assume, therefore, that the water in association does not affect the absorption of the ion. So in general we may say that the absorption maxima of the ion e. g. $(MeCl+5H_2O)^{2+}$ is really the spectrum of a compound $(MeCl)^{2+}$. We have now to explain how it happens that the absorption maxima of such a compound $(MeCl)^{2+}$ correspond to the spectrum of the free Me^{2+} ion. This we shall do by taking an example of $(MeCl)^+$. We make a plausible assumption that molecules of the type $(MeCl)^+$ etc. are very unstable. This gives us an explanation which is clear from the following potential energy diagram, connecting the inter-nuclear distances r with the potential energy U of the molecule in the excited and the unexcited states. The difference between this curve and a similar curve for a normal stable molecule is that in this case D and D' are very much smaller than either the atomic term differences of the dissociation products or the molecular term differences of the molecule itself.

Me (excited)+Cl

(Me Cl)'
excited

Molecular band $h\nu$

atomic line $h\nu^1$

Me (Ground state)+Cl

(Me Cl)'.
Normal

r

D and D′ being small quantities their difference D – D′ will be still smaller. The smaller this quantity becomes the more will $h\nu - h\nu^1$ tend to be equal. Thus it will be clear that the agreement observed, if definitely established, finds an easy explanation.

The salts containing oxygen, viz. $KMnO_4$, $K_2Cr_2O_7$ and Na_2CrO_4 do not show any relation to the term differences of the metal ions concerned. The absorption curve of $KMnO_4$ was also measured by A. Hagenbach and R. Percy in solution and by K. Schnetzler in solid state at low temperatures in the visible region of the spectrum, and a comparison of the three results is shown in the following table.*

Hagenbach & Percy	6370	5707	5470	5252	5054	4865	4701	4510	4395	...
Schnetzler				5537	5312	5102	4911	4735	4567	4414	...
Karim & Samuel...	6250	5700	5410	5210	5040	4780	...	...	...	3140

Here we see that our results coincide fairly well with the measurements of Hagenbach and Percy except that some of the maxima cannot be traced or that they are so much diffused in our curve that we cannot trace them with any great accuracy.

K. Schnetzler has shown that at low temperatures these maxima become real bands, and he treats them as vibrational bands of electronic band system.

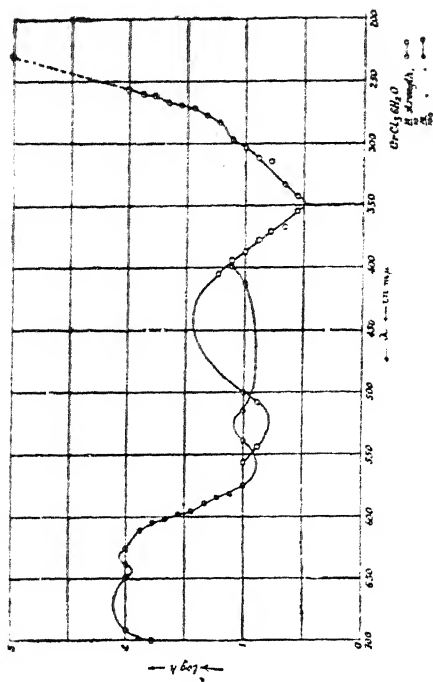*The figures of the above table have been taken from the paper of Schnetzler. Zs. f. Phy. Chem. B. 14, 247, 1931.

Fig. 1. CrCl₃

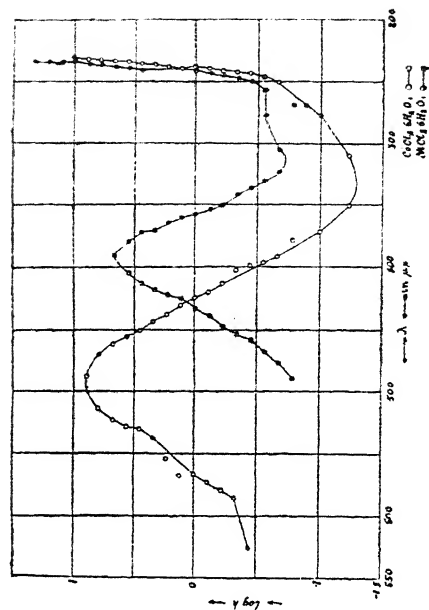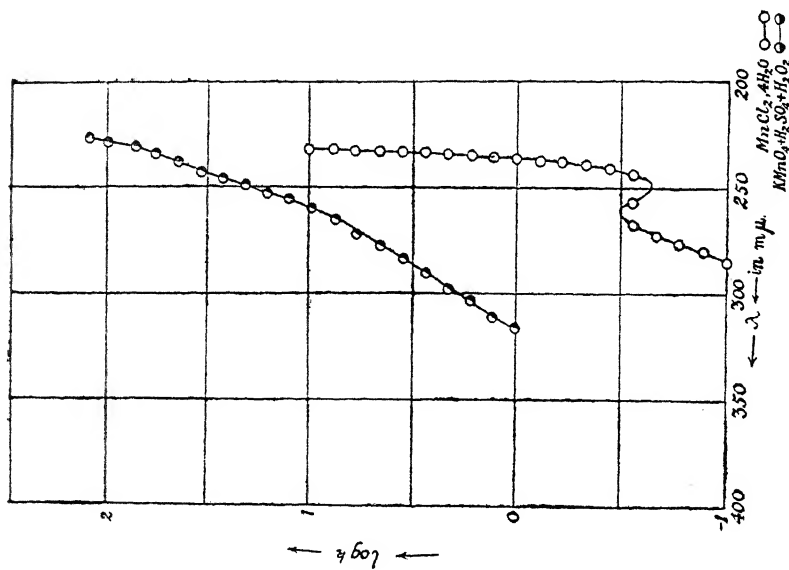Fig. 3. CoCl₂ and NiCl₂

Fig. 2. MnCl₂

It is to be noted that all these bands belong to one main maximum in the solution. Apparently in the solution the distribution of the molecules over these vibrational states are quite different from those in the crystal at low temperatures.

The curves of Na_2CrO_4 and $K_2Cr_2O_7$ are very similar, so that we may assume that the main absorbing ion is the same in both the cases, probably $HCrO_4$. The difference in the height of the maxima of the two curves can also be explained by the fact that the one contains double the number of Cr atoms than the other and has therefore double the probability of forming $HCrO_4$ ions. These curves and especially the many bands of the $KMnO_4$, show no similarity with the absorption bands either of the simple salts treated above or the absorption bands of the complex salts treated in other papers of this series.

TABLE I. $CrCl_3$

MAX OF ABSORPTION OF $CrCl_3$ IN WATER		EMISSION SPECTRA OF Cr.					
		Cr IV Ground level ^4F		Cr III Ground level ^5D		Cr II Ground level ^6S	
$\lambda m\mu$	r cm^{-1} approx	r cm^{-1}	Combin	r cm^{-1} approx	Comb.	r cm^{-1}	Comb.
						12500	$^6D - ^6S$.
669	15000	15014	$^4G - ^4F$				
632	16000					16896	$^6P - ^6S$.
605	16500			19000	$^5F - ^5D$	19529	$^6D - ^6S$
527	19000	21027	$^4H - ^4F$			20514	$^6G - ^6S$
						21824	$^6D - ^6S$
440	22700			21000	$^5G - ^5D$		
						Many more terms. e.g. of combination d^5.	
280	35500					32847	$^6F - ^6S$.

TABLE II. (MnCl$_2$).

MAX OF ABSORPTION OF MnCl$_2$ IN WATER		EMISSION SPECTRA OF Mn			
		Mn IV	Mn III	Mn II Ground level ^{7}S	
λ mμ.	ν cm^{-1} approx			ν cm^{-1}	
				14324	^{5}D – ^{7}S
				38366	^{7}P – ^{7}S
262	38000	?	?	43370	^{5}P – ^{7}S

TABLE III. (YCl$_3$).

MAX. OF ABSORPTION OF YCl$_3$ IN WATER.		EMISSION SPECTRA OF Y		
		Y IV	Y III Ground level ^{2}D	
λ mμ	ν cm^{-1} approx		ν cm^{-1}	
			7466	^{2}S — ^{2}D
265	38000	?	41404	^{2}P — ^{2}D

TABLE IV. (FeCl$_3$)

MAX. OF ABSORPTION OF FeCl$_3$ IN WATER		EMISSION SPECTRA OF Fe			
		Fe IV	Fe III	FeII Ground level ^{6}D	
λ mμ	ν cm^{-1} approx			cm^{-1}	
1020	9800			8846	^{4}D – ^{6}D
790	13000	?	?	13474	^{4}P – ^{6}D
340	29000			20830	^{4}P – ^{6}D
				22637	^{4}F – ^{6}D
				25428	^{4}G – ^{6}D
				31364	^{4}D – ^{6}D

Fig. 1. VCl_3

$VCl_4 + H_2O \rightarrow VCl_3$

λ in $\mu\mu$

$Log\ k$

YCl_3

λ in $\mu\mu$

$Log\ k$
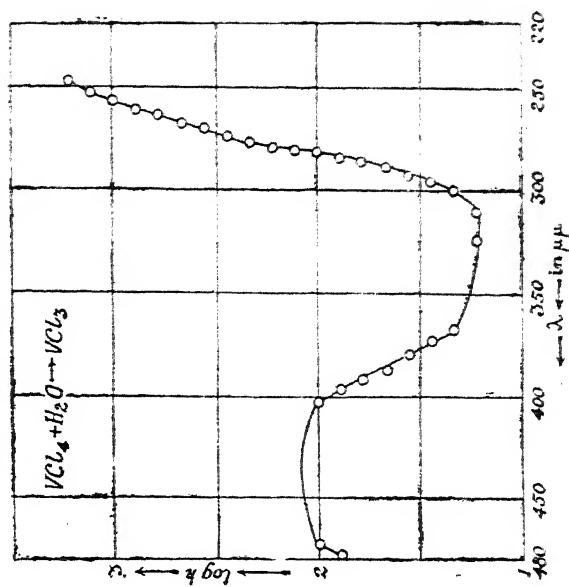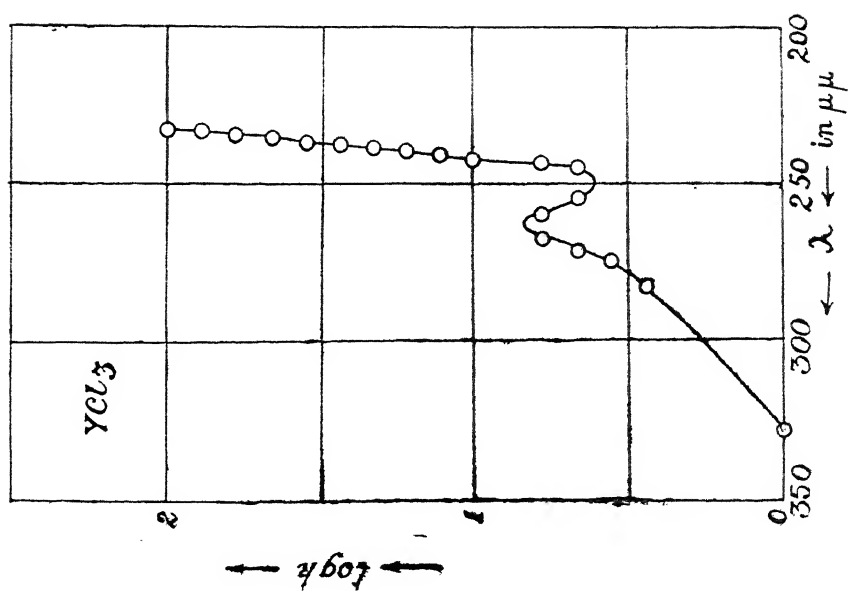
TABLE V. (CoCl$_2$).

Max. of absorption of CoCl$_2$ in Water		Emission spectra of Co			
		Co IV	Co III	Co II Ground Level ^{3}F	
λ mμ	ν cm^{-1} approx			ν cm^{-1}	
1250				5000	^{5}P – ^{3}F
770	12900			10708	^{3}F – ^{3}F
565	17700	?	?	17771	^{5}P – ^{3}F
515	19400				
488	20500				
405	24700				
365	27400				
250?	40000			45197	^{5}F – ^{3}F

TABLE VI. (NiCl$_2$).

Max. of absorption of NiCl$_2$ in water.		Emission spectra of Ni			
		Ni IV	Ni III	Ni II Ground level ^{6}D.	
λ mμ	ν cm^{-1} approx			ν cm^{-1}	
1200				8 - 10000	^{4}F – ^{2}D.
720	13900			13549-	^{2}F – ^{2}D.
445	22500	?	?	14994	
390	25600			23106	^{2}D – ^{2}D.
270	37000				
238	42000				

TABLE VII. (PdCl$_2$).

Max. of absorption of PdCl$_2$ in water.		Emission spectra of Pd.			
		Pd IV	Pd III	Pd II Ground level ^{2}D	
λ mμ	ν cm^{-1} approx			ν cm^{-1}	
456	21900				
350	28600	?	?	25081	^{4}F – ^{2}D
278	35900			32277	^{2}F – ^{2}D
				36281	^{4}P – ^{2}D

FIG. 6.   PdCl$_2$, RhCl$_3$, RuCl$_3$

FIG. 8.   KMnO$_4$

FIG. 7.   IrCl$_4$, OsCl$_4$
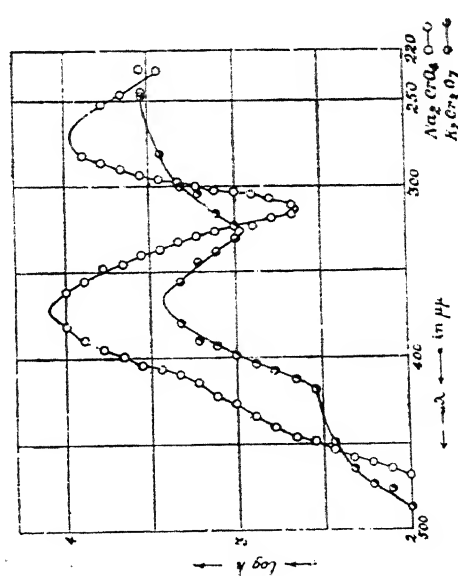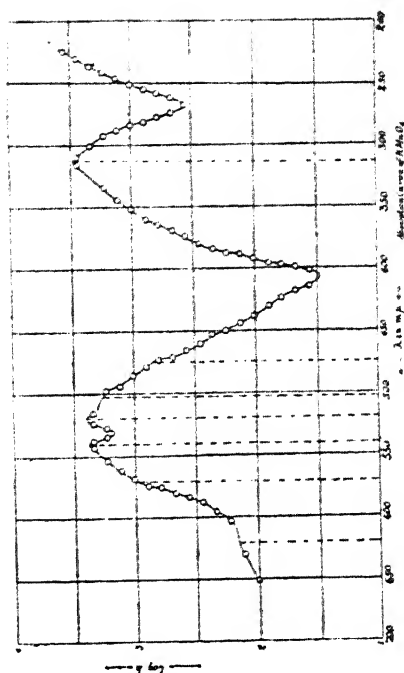
FIG. 9.   Na$_2$CrO$_4$

TABLE VIII. (VCl$_3$).

Max. of absorption of VCl$_2$ in water.		EMISSION SPECTRA OF V.		
		V IV Ground level ^{3}F	V III	
$\lambda\ m\mu$	$\nu\ cm^{-1}$ approx.	$\nu\ cm^{-1}$		
470	21300	19807	^{1}G – ^{3}F	
410	24400	20091	^{1}S – ^{3}F	

Other terms lie in the extreme red and in Infra red.

TABLE IX.

The Emission spectra of RhCl$_3$; IrCl$_6$ and OsCl$_4$ being not yet analysed. only the Maxima of absorption are given below :—

Max. of absorption of RhCl$_3$ in water.		Max. of absorption of IrCl$_4$ in water.		Max. of absorption of OsCl$_4$ in water.	
$\lambda\ m\mu$	$\nu\ cm^{-1}$ approx.	$\lambda\ m\mu$	$\nu\ cm^{-1}$ approx.	$\lambda\ m\mu$	$\nu\ cm^{-1}$ approx.
370	27000	485	20600		
350	28600	429	23300		
		408	24500	373	26700
311	32100	280	35700		

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